Comparison of the herbicidal activities of compound **1**, with no branching, and compound **2** indicates that introduction of a methyl group results in a considerable increase in herbicidal activity (Table 1); however, compound **2** does not show selectivity towards rice. Compound **4**, with a monofluoromethyl group, has similar activity to compound **2** but shows less damage to rice. Replacement of a monofluromethyl with a difluoromethyl or a monochloromethyl group (compounds **5** and **6**, respectively) results in decreased herbicidal activity.

Introduction of a fluoroethyl group produces the two diastereoisomers **7** and **8** which can be separated easily by chromatography at the sulfonamide intermediate stage. The relative stereochemistry of **7** was assigned from X-ray crystallographic study of the corresponding *tert*-butyl sulfonamide single crystal as *erythro*.[5] This *erythro* isomer exhibits a high level of activity against several annual and perennial paddy field weeds and low activity against transplanted rice. It is particularly active against barnyardgrass, which is the main problem weed in paddy fields. Of the two diastereoisomers, the *erythro* form (**7**) is more active than the *threo*- form **8**.

We next focused on the effect of aromatic ring substitution on herbicidal activity. A fluorine substituent at the 6-position on the phenyl ring gave compound **9** with similar activity to that of compound 7. However, introduction of the strongly electron-donating dimethylamino group at this position (compound **10**) resulted in reduced activity. Introduction of a strongly electron-withdrawing group in the 5-position (compound **11**) resulted in a complete absence of activity at $50\,\mathrm{g\,ha^{-1}}$, while the introduction of the electron-donating methoxy group at position **5** (compound **12**) resulted in moderate activity. A (electron-withdrawing) fluoro group at positions such as **4** and **5** in the phenyl ring resulted in diminished activity (compounds **13** and **14**, respectively).

In conclusion, fluoroalkyl hydroxymethylsulfonylureas represent a new class of sulfonylurea herbicide with high activity. Of the various derivatives tested, the *erythro*-fluoroethyl compound (coded K11451) showed excellent herbicidal activity against several annual and perennial paddy weeds, including barnyardgrass, and caused little damage to transplanted rice.

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Herbicidal and biological characteristics of a new benzenesulfonylurea compound K-11451 under submerged paddy conditions

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Abstract: The new benzenesulfonylurea K-11451, an α-hydroxy-β-fluoropropyl- compound, applied at 3–9 g ha $^{-1}$, controlled annual and perennial weeds grown in submerged paddy soil under greenhouse conditions. It effectively controlled barnyardgrass at growth stages varying from pre-emergence to the five-leaf stage. The compound inhibited acetolactate synthase, I_{50} values for the enzyme isolated from barnyardgrass and rice being 56 and 67 nM, respectively. K-11451 inhibited the growth of rice when it was transplanted at a shallow depth (0–1 cm) and water leaching from the paddy soil was high (3–5 cm per day). With a water depth of 3 cm, the compound appeared to move readily down into the paddy soil and had the relatively short half-life of 15.2 days under submerged paddy conditions. A mixture of K-11451 + mefenecet + daimuron (9 + 250 + 250 g ha^{-1}) controlled almost all weeds in the paddy field without injury to rice, so that the combination could be used as a 'one-shot' herbicide in rice culture.

Keywords: acetolactate synthase; barnyardgrass; benzenesulfonylurea; daimuron; leaching; mefenecet; one-shot herbicide; rice

Sulfonylurea herbicides are highly active at low application rates, control a wide spectrum of weeds and have favourable toxicological properties. They are also safe to use in a number of major crops including rice. The sulfonylureas, along with imidazolinones and triazolopyrimidines, are acetolactate synthase (ALS) inhibitors,[1] KIH-2023[2] and LGC-40863[3] being examples of success in this area.

Barnyard grass (*Echinochloa* spp) is one of the most troublesome weeds in paddy fields world-wide; infestations with this weed cause severe yield loss and quality reduction in rice culture[4] so that rice growers anxiously await a new herbicide to control it, as well as other annual and perennial weeds.

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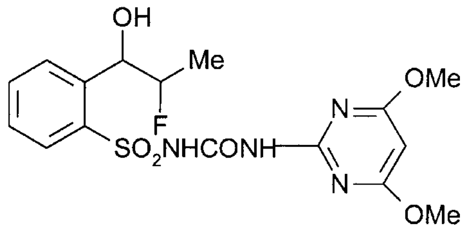

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Figure 1. Chemical structure of K-11451.

K-11451 (Fig 1), a new benzenesulfonylurea with an α-hydroxy-β-fluoropropyl moiety, gave excellent control of major problem weeds in paddy fields, especially of barnyardgrass, under submerged paddy conditions in greenhouse trials (Table 1). At application rates of 3–9 g AI ha^{-1} it effectively controlled the annual weeds *Echinochloa oryzicola* Ohwi, *Scirpus juncoides* Roxb, *Monochoria vaginalis* Presl and *Lindernia procumbens* Philcox and the perennial weeds *Cyperus serotinus* Rottb, *Sagittaria pygmaea* Miq., *Eleocharis kuroguwai* Ohwi, *Potamogeton distinctus* Benn and *Sagittaria trifolia* L (Table 1). K-11451 was more effective than the sulfonylurea herbicides registered for use in the rice crop (pyrazosulfuron-ethyl, bensulfuron-methyl, cinosulfuron) for the control of barnyardgrass at various growth stages up to the five-leaf stage, with good compatability to the rice itself: at 20 g AI ha^{-1} (soil treatment) it completely controlled barnyardgrass at the four-to five-leaf stage.

K-11451 inhibited the activity of ALS, I_{50} values for the enzyme extracted from barnyardgrass and rice plants being 56 and 67 nM, respectively; corresponding I_{50} values for pyrazosulfuron-ethyl and benzsulfuron-methyl were 63 nM and 86 nM (barnyard grass) and 6 nM and 9.4 nM (rice), respectively. Therefore the selectivity of K-11451 between barnyardgrass and rice is not due to differential susceptibilities of ALS extracted from the two species but to other factors; crop selectivity with ALS inhibitors has been shown to be associated with metabolic detoxification in all cases investigated to date.[1]

The efficacy of K-11451 and its selectivity were further examined under various submerged paddy conditions. When applied to direct-seeded rice before the two-leaf stage (eight days after seeding) the growth of rice was slightly inhibited but the plants had recovered by three weeks after application of the herbicide in that plant height was almost the same as that in untreated plants, even with application rates from 20 to 40 g ha^{-1}. There was also some inhibition of growth with rice plants transplanted at a shallow

Table 1. Herbicidal activities of K-11451, of some commercialy available sulfonylureas and of mixtures against rice and major weed species in greenhouse tests incorporating submerged paddy field conditions.

				Activity (% damage)									
		Rice[b]		*Annual weeds*[c]					*Perennial weeds*[d]				
Compound	*Rate*[a] ($g\,ha^{-1}$)	*Seed*	*3-leaf*	*Ec*	*Sj*	*Mv*	*Ak*	*Lp*	*Cs*	*Sp*	*Ek*	*Pd*	*St*
K-11451	3	10	0	70	100	100	0	50	60	90	100	100	80
	6	30	0	90	100	100	0	70	100	95	100	100	90
	9	50	20	100	100	100	0	100	100	95	100	100	100
	18	60	40	100	100	100	0	100	100	95	100	100	100
Pyrazosulfuron-ethyl	10	0	0	50	100	100	0	100	100	95	100	100	100
	20	15	0	80	100	100	0	100	100	95	100	100	100
	40	50	10	100	100	100	0	100	100	95	100	100	100
Bensulfuron-methyl	20	0	0	0	70	100	0	70	90	90	80	70	70
	40	10	0	30	90	100	0	95	90	90	90	90	90
	80	40	20	60	95	100	30	100	100	100	90	90	90
Cinosulfuron	20	0	0	20	80	100	30	90	90	90	90	90	90
	40	50	0	70	90	100	30	95	95	90	90	90	95
	80	70	30	80	95	100	40	100	100	95	90	95	100
K-11451	9+250	5	0	100	100	100	0	100	100	95	100	100	100
+diamuron	18+500	20	10	100	100	100	0	100	100	100	100	100	100
K-11451	9+250	40	10	100	100	100	90	100	100	95	100	100	95
+mefenacet	18+500	60	40	100	100	100	100	100	100	100	100	100	100
K-114551 +diamuron +mefenacet	9+250+250	10	0	100	100	100	100	100	100	100	100	100	100

[a] Herbicides applied as a soil application seven days after seeding or transplanting.

[b] Planted as seed or transplanted at three-leaf stage.

[c] E c, *Echinocloa oryzicola*; Sj, *Scirpus juncoides*; M v, *Monarchia vaginalis*; A k, *Aneilema keisak*; L p, *Lindermia procumbens*.

[d] Cs, *Cyperus serotinus*; S p, *Sagittaria pygmaea*; E k, *Eleocharis kuroguwai*; P d, *Potamogeton distinctus*; S t, *Sagittaria trifolia*.

(0–1 cm) depth and when water leaching from paddy soil was high (3–4 cm).

The downward movement of K-11451 in paddy soil was investigated by adding the compound at rates varying from 1.56 to 50 g ha^{-1} to the top of a column of paddy soil (10 cm) from which water subsequently leached at 3 cm per day. After 24 h leaching, the soil column was divided into 1-cm sections, starting at the top, and barnyardgrass seeds were planted in each section. Measurements of the extent of growth of the weed indicated that the compound had moved readily to a depth of 3 cm. The half-life of K-11451, estimated in a pot test using Gerber's method,[5] was relatively short, being 15.2 days under submerged paddy conditions.

It has been reported that phytotoxic effects of several sulfonylurea compounds on rice can be reduced by using slow-release formulations and by using them as a mixture with daimuron.[6] The safety of treated direct-seeded or transplanted rice was increased when K-11451 was applied at 9 or 18 g ha^{-1} either once as a slow-release formulation or with daily applications of 5.0, 4.0 or 3.3% of the total amount. It was also increased when K-11451 was applied in admixture with daimuron; for example, K-11451 + daimuron at 9 + 250 g AI ha^{-1}, gave complete control of annual weeds, except *Aneilema keisak* Hassk, in a greenhouse trial, without injury to the rice (Table 1). It is well known that *A keisak* cannot be controlled adequately with sulfonylurea herbicides, including K-11451, so that control of this weed without damage to rice would require mixtures with other herbicides. Of a number of mixtures, the combination of K-11451 with mefenacet and daimuron (9 + 250 + 250 g AI ha^{-1}) provided the best results. Thus such a combination could be used successfully as a one-shot herbicide in rice culture.

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Chloroacetanilides, oxyacetamides, tetrazolinones: mode of action. 1. Cross resistance and oleic acid incorporation in algal model systems

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Abstract: Results presented suggest that chloroacetamides, oxyacetamides, tetrazolinones, and possibly cafenstrole, act at the same site, although the precise molecular mode of action is still unknown, despite much research effort.

Keywords: herbicides; chloroacetanilides; oxyacetamides; tetrazolinones; oleic acid incorporation; mefenacet; BAY FOE 5043; BAY YRC 2388; cafenstrole

1 INTRODUCTION

In 1984, oxyacetamide herbicide chemistry was first introduced with the herbicide mefenacet, used mainly for the control of *Echinochloa* species in rice.[1] In 1995, the oxyacetamide BAY FOE 5043 was added as a second herbicide from this group, this time for weed control in corn, soybean and cereals.[2] The first commercial tetrazolinone herbicide will be BAY YRC 2388, which was introduced for applications similar to those of mefenacet in 1997.[3]

Extensive studies on the mode of action of mefenacet have shown close similarities with chloroacetanilide herbicides, e g alachlor. The results and effects obtained with mefenacet have now been reproduced with BAY FOE 5043, BAY YRC 2388, and also with cafenstrole. These are:

1. Inhibition of mitotic entry in oat roots.[4]
2. Inhibition of cell division in the green alga *Chlamydomonas reinhardtii* Dang.[5]
3. Symptomology in corn: strong plant stunting and leaf curling.
4. Complete reversal of the inhibitory effects in corn by simultaneous treatment with dichloroacetamide safeners.
5. Metabolism in corn by glutathione conjugation, particularly in safened plants, suggests facile nucleophilic displacement (not studied for cafenstrole).
6. Plant sensitivity microtests aimed at defining the relevant mode of action group place the oxyacetamides, tetrazolinones and cafenstrole with the chloroacetamides.[6]

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